

Correlation and Prediction of Physical Properties Using Step Potential Equilibria and Dynamics (SPEAD)

Z.N. Gerek, O. Unlu, N. Gray, and J.R. Elliott^{C,S}

*Chemical Engineering Department
The University of Akron
Akron, OH 44325-3906, U.S.A.*

The Step Potential Equilibria And Dynamics (SPEAD) model provides a basis for molecular modeling of thermodynamic and transport properties. It is based on Discontinuous Molecular Dynamics (DMD) and second order Thermodynamic Perturbation Theory (TPT). DMD simulation is applied to the repulsive part of the potential, complete with molecular details like interpenetration of the interaction sites, 110° bond angles, branching, and rings. The thermodynamic effects of disperse attractions and hydrogen bonding are treated by perturbation theory. This approach accelerates the molecular simulations in general and the parameterization of the force field in particular.

The approach is fundamentally based on a stepwise characterization of the disperse interactions and Wertheim potentials for the hydrogen bonding. The force field characterization of straight and branched alkanes, aromatics, alcohols and ethers based on accurately correlating experimental vapor pressures, densities, and internal energies with those computed by SPEAD have been demonstrated. The characterizations of the molecular interactions are transferable and the predictions of vapor pressure are more accurate than previous transferable potential models, to the best of our knowledge. The same methodology is applied to esters, ketones, sulfides, and thiols in the present work.

When using transferable potentials, we obtained average deviations of roughly 9% for vapor pressure and 2% for liquid density. Correlations of mixture thermodynamics are generally accurate to 10% in bubble pressure, even for complex mixtures.

The methodology is straightforwardly extended to correlation and prediction of transport properties since it involves molecular dynamics. The primary concern is that 30-100 ns of simulated time (~3 CPU days for large molecules) are necessary to reliably characterize viscosity. In the present work, empirical correlations are presented for correcting the transport properties derived from the purely repulsive simulations.